

Observation of Spin Freezing in CaV_4O_9 and CaV_2O_5 by μSR

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(February 1, 2008)

Abstract

We have performed muon spin relaxation and susceptibility measurements of CaV_4O_9 and CaV_2O_5 , systems in which spin gap-like behavior has been found. We observe spin freezing in the two compounds below 12 K and 50 K, respectively. Our results indicate the possibility that a substantial fraction of the vanadium magnetic moment is not in a spin singlet state at low temperatures in either material.

75.50.Lk, 76.75.+i

The properties of low dimensional and/or frustrated magnetic materials have attracted considerable attention due to the appearance of various non-Néel ground states. Systems with singlet ground states and spin gaps include the one-dimensional Haldane (integer spin chain, *eg.* Y_2BaNiO_5) and spin-Peierls (spin 1/2 chain, *eg.* CuGeO_3) states. Spin ladders with even numbers of legs (such as SrCu_2O_3) can also have spin singlet ground states. Recently, a possible new type of singlet ground state, the plaquette resonating valence bond (PRVB) state, where the singlet is comprised of four spins in a two dimensional arrangement, has received considerable theoretical attention [1–9] since the proposal by Taniguchi *et al.* [10] that CaV_4O_9 possesses such a ground state.

$\text{AV}_n\text{O}_{2n+1}$ ($n = 2, 3, 4$, $\text{A}=\text{Ca}, \text{Na}, \text{Sr}$) is a series of related compounds in which stacked layers of edge sharing VO_5 pyramids form an essentially square lattice in which $1/(n+1)$ of the spin-1/2 V lattice points are periodically depleted. [11] An extremely interesting feature of these vanadates is that they offer the possibility of studying several different magnetic ground states in a family of related compounds. In CaV_3O_7 ($n = 3$) all the vanadium ions are in the spin 1/2 V^{4+} state and order antiferromagnetically [12,13]. In CaV_2O_5 the V^{4+} ions are arranged in the two leg ladder structure while spins in adjacent ladders are coupled via a zig-zag chain structure. A spin gap has been inferred from NMR and susceptibility in CaV_2O_5 , although its microscopic origin isn't clear, as it is unknown which exchange interaction (ladder or zig-zag) is dominant [14]. The structure of NaV_2O_5 is similar to that of CaV_2O_5 , except that half of the V ions are V^{4+} (spin 1/2) while the other half are V^{5+} (spin 0), resulting in a 1-d chain structure; a spin-Peierls transition at 34 K (the highest yet observed) has recently been identified [15]. Susceptibility [10], NMR- $1/T_1$ [10,16,17] and inelastic neutron scattering [17] measurements of CaV_4O_9 ($n = 4$) have indicated the presence of a spin gap which has generated considerable theoretical interest as this would be the first two dimensional system with a spin singlet ground state.

The first proposed mechanism for the singlet state in CaV_4O_9 was the plaquette resonating valence bond (PRVB) state, which consists of local singlets from the four spins on a nearest or next-nearest neighbour plaquette. Depending on the strength of the various exchange

interactions, different ground states, including Néel order, dimerization and the PRVB state have been found theoretically; several authors have argued that frustration effects select the PRVB state. Orbital ordering has been suggested as a spin gap mechanism in both CaV_2O_5 and CaV_4O_9 [18]. However, in the case of CaV_4O_9 , this suggestion appears to be inconsistent with neutron [17] and susceptibility [19] measurements.

Ceramic specimens of CaV_4O_9 and CaV_2O_5 were grown at Nagoya University and ISSP respectively, as described previously [10,14]. Field-cooled susceptibility measurements are shown in Fig. 1. For CaV_4O_9 , χ shows a broad maximum around 100K, then drops rapidly with decreasing temperature, while for CaV_2O_5 , χ peaks above room temperature then becomes essentially temperature independent below about 80 K. A weak Curie term in both samples at low temperatures corresponds to an impurity level of $\sim 0.1\%$ V^{4+} free moments.

We performed detailed dc-susceptibility measurements to search for irreversibility (a signature of spin glass order) in both samples. We first cooled in zero field to 5 K, applied a magnetic field, then took measurements in increasing temperature up to room temperature, and then upon cooling to low temperatures. No irreversibility was observed in fields of 100 G, 1000 G or 1 T for CaV_4O_9 . In the case of CaV_2O_5 , we found that irreversibility set in at about 50 K, as shown in Fig. 1. We performed this measurement sequence in a series of fields, finding that the irreversibility was greatest in an applied field of roughly 1 kG. The degree of irreversibility depended on the field as well as the time delay at each point, with a maximum of about 15 % for the fractional change in the moment. Irreversibility of greater than 2 % was apparent for fields between 500 G and 1 T.

Muon spin relaxation (μSR) is an extremely sensitive magnetic probe. Internal magnetic fields of several gauss (corresponding to typical static moments less than $0.1 \mu_B$) are readily detected. As a real-space probe, μSR can sensitively determine ordered volume fractions and is especially powerful for the study of disordered magnetic materials such as spin glasses. The specimens were mounted on a pure silver sample holder in either a helium gas flow cryostat or dilution refrigerator at the M13 and M15 surface muon channels at TRIUMF. Spectra were measured in zero field and longitudinal field geometries.

We had anticipated confirming the non-magnetic ground state in CaV_4O_9 and CaV_2O_5 by observing only weak, temperature-independent muon spin relaxation from static nuclear dipole moments and possibly some weak dynamic relaxation due to free moments associated with local defects in the singlet ground state as in our previous studies of other spin singlet systems [22–24]. Instead, below 100 K in CaV_4O_9 and 150 K in CaV_2O_5 , we observed increasingly strong dynamic relaxation in both zero field and in an applied longitudinal field as shown in Fig. 2a for CaV_4O_9 ; spectra for CaV_2O_5 are qualitatively similar. In both materials the relaxation rate increased with decreasing temperature, indicating the slowing down of fluctuating paramagnetic moments. Above 15 K in CaV_4O_9 and 80 K in CaV_2O_5 , the relaxation was exponential while it decayed with a two component form at lower temperatures.

Fig. 3 shows the relaxation rates for the two vanadates in both low field (zero field or 100 G) and high field (3000 G in CaV_4O_9 and 1000 G in CaV_2O_5). Filled symbols are fits to a single exponential relaxation rate (used for all fields at higher temperatures and low fields at low temperature) while open symbols are the relaxation rate of the longer-lived tail component (which reflects the effects of fluctuating fields) in high fields at lower temperatures. The relaxation rate of the longer-lived component reaches a maximum value at 50 K in CaV_2O_5 and at 12 K in CaV_4O_9 , then decreases with decreasing temperature. The weak field dependence at high temperature is characteristic of a paramagnetic state, while the two component form, where the application of a longitudinal field decouples the fast relaxing signal, increasing the amplitude of the slowly relaxing component (as shown in Fig. 2b), indicates that the source of the relaxation at low temperatures in both materials is a quasi-static distribution of internal magnetic fields, such as is found in a spin glass. All of this behavior seen in μSR indicates that CaV_4O_9 and CaV_2O_5 undergo spin freezing below 12 K and 50 K, respectively.

In both materials, the amplitude of the relaxing signal indicates that essentially the entire volume fraction ($> 95\%$) is involved in the spin freezing. We can estimate the magnitude of the characteristic quasi-static internal fields at low temperatures from the zero/low field

relaxation rates, obtaining $20 \mu\text{s}^{-1}/\gamma_\mu \sim 250 \text{ G}$ for CaV_4O_9 and $65 \mu\text{s}^{-1}/\gamma_\mu \sim 760 \text{ G}$ for CaV_2O_5 .

In the paramagnetic regime, the muon spin relaxation rate in an applied longitudinal field $B_L = \frac{\omega_L}{\gamma_\mu}$ due to electronic moments fluctuating with an inverse correlation time ν is given by

$$1/T_1 = \frac{\gamma_\mu^2 B_{\text{inst}}^2 \nu}{\nu^2 + \omega_L^2}, \quad \nu \gg \gamma_\mu B_{\text{inst}} \quad (1)$$

where B_{inst} is the average size of the instantaneous local field, $\gamma_\mu = 85.1 \text{ kHz/G}$ is the muon gyromagnetic ratio. Measurement of $1/T_1$ for several fields at the same temperature allows the simultaneous determination of B_{inst} and ν .

We attempted to use Eqn. 1 to calculate the size and fluctuation rate of the local fields in CaV_2O_5 above 50 K. However, we found that the relaxation rate actually increased with increasing field around 1 kG, which is inconsistent with the expected behavior for paramagnetic moments. This effect indicates that the application of the field actually enhanced the slowing down of the fluctuations. If the spin freezing depends on the frustration of antiferromagnetic interactions by competing ferromagnetic interactions, then the application of a field could enhance this and promote spin freezing.

We measured the $1/T_1$ relaxation rate in CaV_4O_9 for a range of applied fields between 100 G and 3500 G, at five temperatures between 18 K and 30 K (shown in Fig. 4). Fitting $1/T_1$ to Eqn. 1 for each temperature independently we obtained $\gamma_\mu B_{\text{inst}} = 21 \pm 0.3 \mu\text{s}^{-1}$ for each. This value of B_{inst} also agreed with the static local field seen at low temperature in this material, indicating that there is no change in the size of the moments responsible for the spin relaxation between 2 K and 30 K. Using this value of B_{inst} , we obtain the temperature dependence of the fluctuation rate ν , shown in the inset of Fig. 4.

The fluctuation rate ν increases quickly with increasing temperature at low temperatures, then eventually begins to saturate at higher temperatures. As shown in the inset of Fig. 4, we can fit the entire temperature dependence with the phenomenological form:

$$\nu = \nu_\infty \frac{1}{e^{\Delta/kT} + 1} \quad (2)$$

where we find $\nu_\infty = (3.0 \pm 0.3) \times 10^{10} \text{ s}^{-1}$ and $\Delta = 114 \pm 3 \text{ K}$. This form would be reasonable if the fluctuation rate were determined by the thermal population of some excited state, with an energy gap Δ above the ground state. The gap value that we obtain is in good agreement with the values seen with susceptibility, NMR and inelastic neutron scattering which suggests that we are observing spin dynamics which are coupled to those seen in those techniques. However, the overall behaviour we see is different from these other techniques: for example, the relaxation rate in NMR decreases with decreasing temperature, here, it increases.

The temperature dependence of ν given by Eqn. 2 would be expected if there were two different spin systems, one which relaxed the other. As the subsystem causing the cross-relaxation were gapped, then the remaining subsystem would no longer be relaxed and could undergo slowing down and eventual spin freezing. Additional evidence for the presence of two different spin subsystems is the slow fluctuation rate $\nu_\infty = 3 \times 10^{10} \text{ s}^{-1}$, much lower than estimates of the exchange frequencies ($\sim 3 \times 10^{12} \text{ s}^{-1}$) in these materials.

Our observations of slowing down of paramagnetic spin fluctuations over a wide temperature range and spin freezing below 12 K in CaV_4O_9 and 50 K in CaV_2O_5 are at first difficult to reconcile with a picture of a simple spin singlet ground state in the two systems. The size of the characteristic local fields in the two compounds (250 G and 760 G, respectively) are comparable in magnitude to the uniform fields seen in the antiferromagnetic state of CaV_3O_7 (600 G and 1.5 kG for the two muon sites in that material). Since each V^{4+} spin in CaV_3O_7 has an ordered moment of roughly $0.4 \mu_B$, [13] we see that a sizable fraction of the V moments in CaV_4O_9 and CaV_2O_5 must have frozen moments on the order of $0.1 \mu_B$. Thus, we can exclude the possibility of spin freezing of dilute impurities (such as seen in susceptibility) causing the observed phenomena. One might imagine that the implanted muons could act as impurities and induce spins around the muon. However, such a case has not been seen in other singlet systems, including Haldane, spin-Peierls or copper based spin ladders. If spins are actually induced by the muons it would indicate an extremely sensitive nature of the ground state of the host spin systems. The observation of irreversibility in

the susceptibility of CaV_2O_5 at the same temperature as the spin freezing in μSR argues against the possibility of a muon-induced effect in that compound.

A similar situation arose in studies of the two leg ladder system $\text{LaCuO}_{2.5}$, where spin gap behavior (with $\Delta = 474$ K) was seen in susceptibility measurements [25]. However, NMR and μSR measurements found magnetic ordering below $T_N = 120$ K [26]. Subsequent theoretical calculations [27] showed that near the quantum critical point of a transition to a spin liquid $\chi(T) = \chi_0 + aT^2$, where χ_0 can be small. As a result, one observes a large decrease in χ which mimics a spin gap, yet still finds a substantial ordered moment. Calculations of the unfrustrated CaV_4O_9 lattice find Néel order [4] for a wide range of couplings yet the calculated $\chi(T)$ would be difficult to distinguish from a true gap due to experimental difficulties in determining $\chi_{\text{spin}} = 0$ in the presence of temperature-independent contributions (Van-Vleck, core diamagnetism etc.) and Curie-like impurity contributions.

Inelastic neutron scattering measurements of CaV_4O_9 have exhibited clear gap-like behavior [17]. However, those results do not exclude the existence of the frozen moment seen in the present study; the slow fluctuations and freezing we observe would be at too low energy to have been detected in the neutron measurements. Spin freezing should be apparent in NMR measurements of both systems. In fact, ^{51}V NMR measurements of CaV_4O_9 deviate from their activated form around 15 K, although this was attributed to impurities. Our results indicate this effect may be intrinsic. A potential complication in comparing μSR and NMR measurements is that the NMR experiments were performed in high magnetic field (7T) which may affect the low temperature properties. Zero field NQR measurements could provide valuable additional information.

Our observation of spin freezing involving a substantial moment in both CaV_4O_9 and CaV_2O_5 implies that the ground state of both systems is more complicated than the spin singlets which have been proposed to date. In CaV_4O_9 , we see evidence for the presence of two spin systems: one of which is gapped while the other undergoes spin freezing. It remains to be seen whether the different subsystems correspond to distinct vanadium spins, or to different portions of each vanadium moment.

We appreciate the assistance of Syd Kreitzman, Bassam Hitti and the TRIUMF- μ SR User Facility. Work at Columbia was supported by NSF-DMR-95-10453, 10454 and NEDO (Japan).

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FIGURES

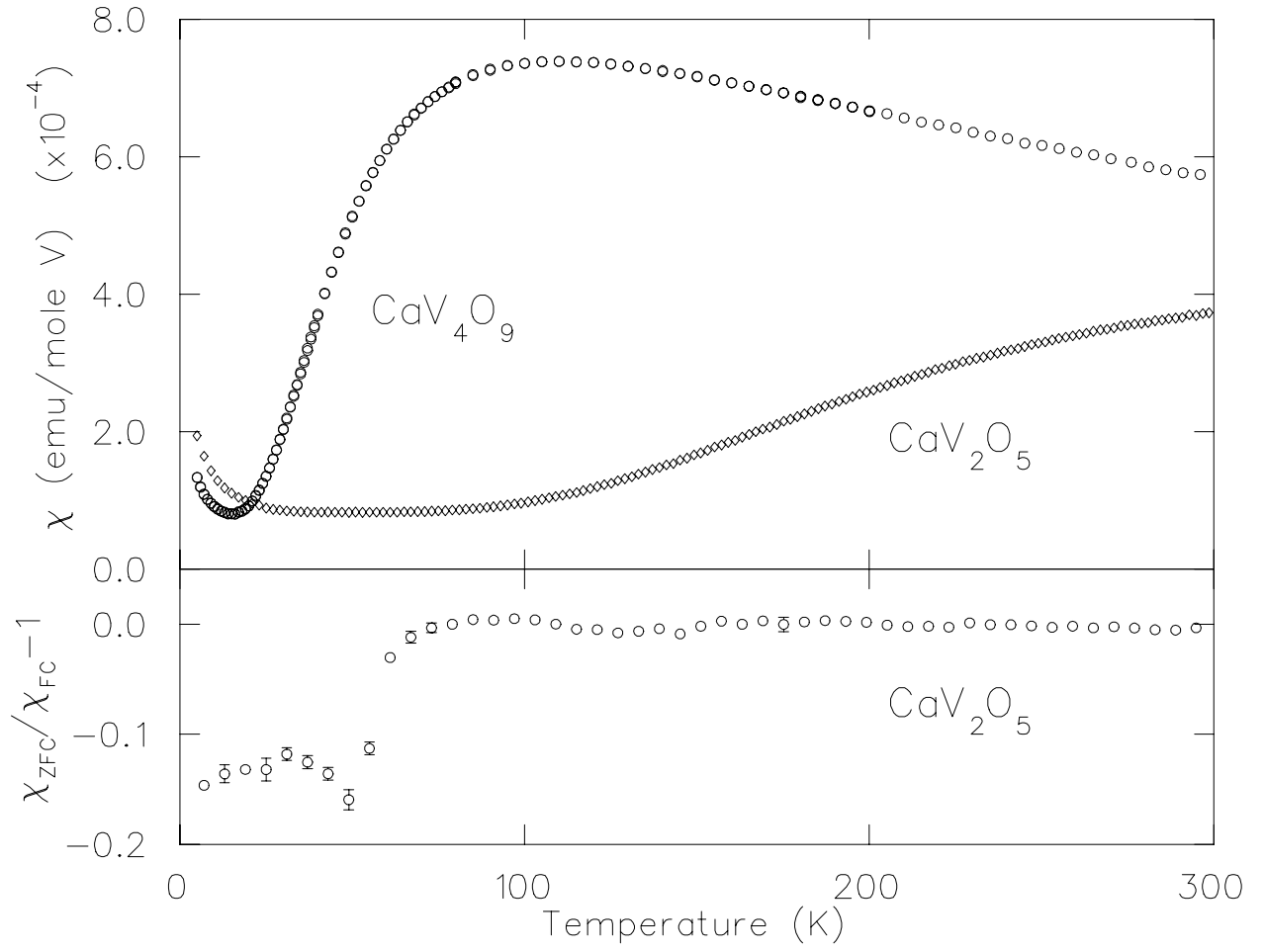


FIG. 1. (a)Magnetic susceptibilities of CaV_4O_9 and CaV_2O_5 and (b) Fractional irreversibility $(\chi_{\text{ZFC}}/\chi_{\text{FC}} - 1)$ in CaV_2O_5 .

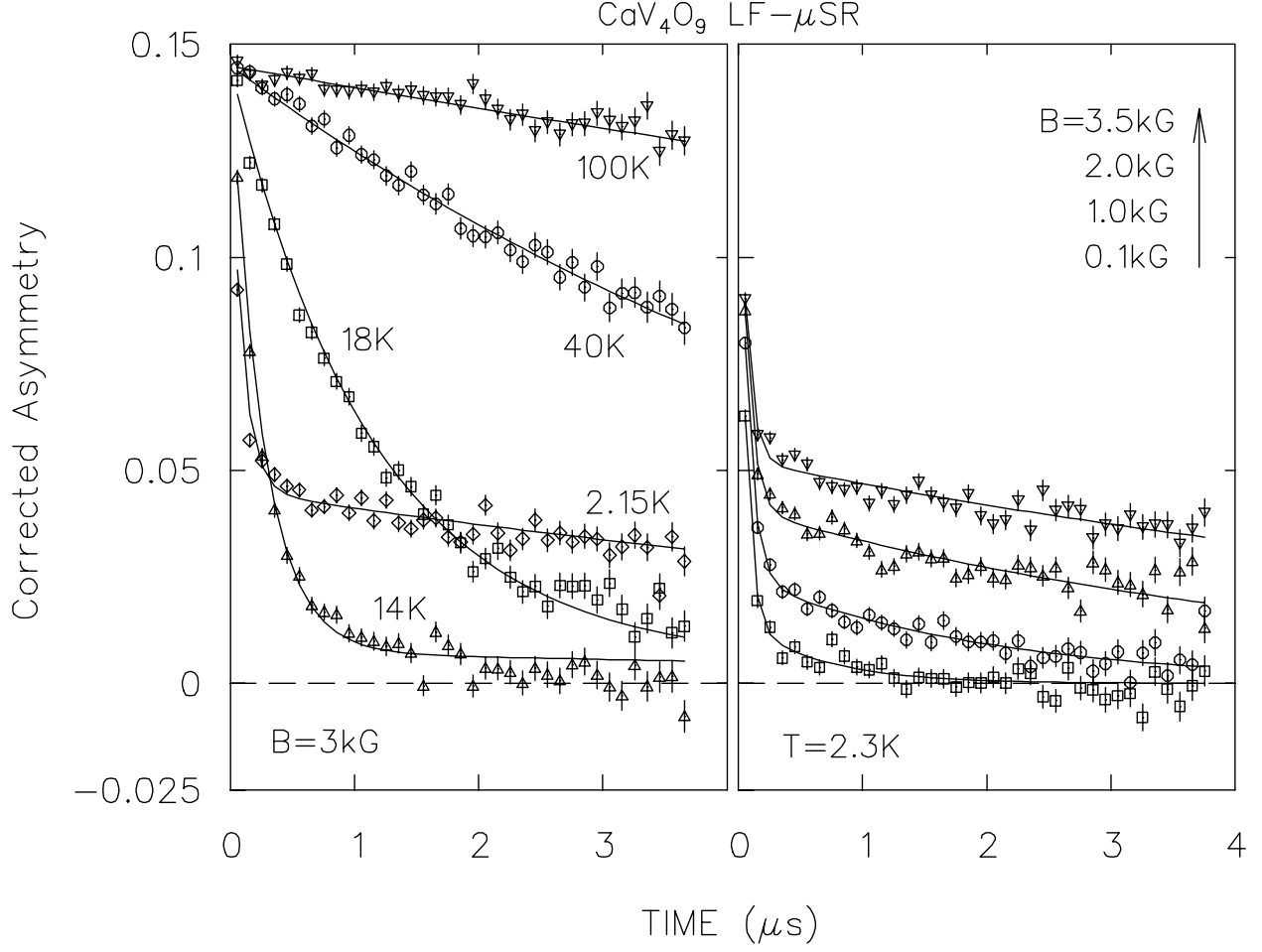


FIG. 2. (a)LF- μ SR spectra measured in $B=3000$ G for CaV_4O_9 for $T=100$ K, 40 K, 18 K, 14 K and 2.15 K and (b)LF- μ SR spectra measured at 2.3 K in CaV_4O_9 for $B=100$ G, 1000 G, 2000 G and 3500 G.

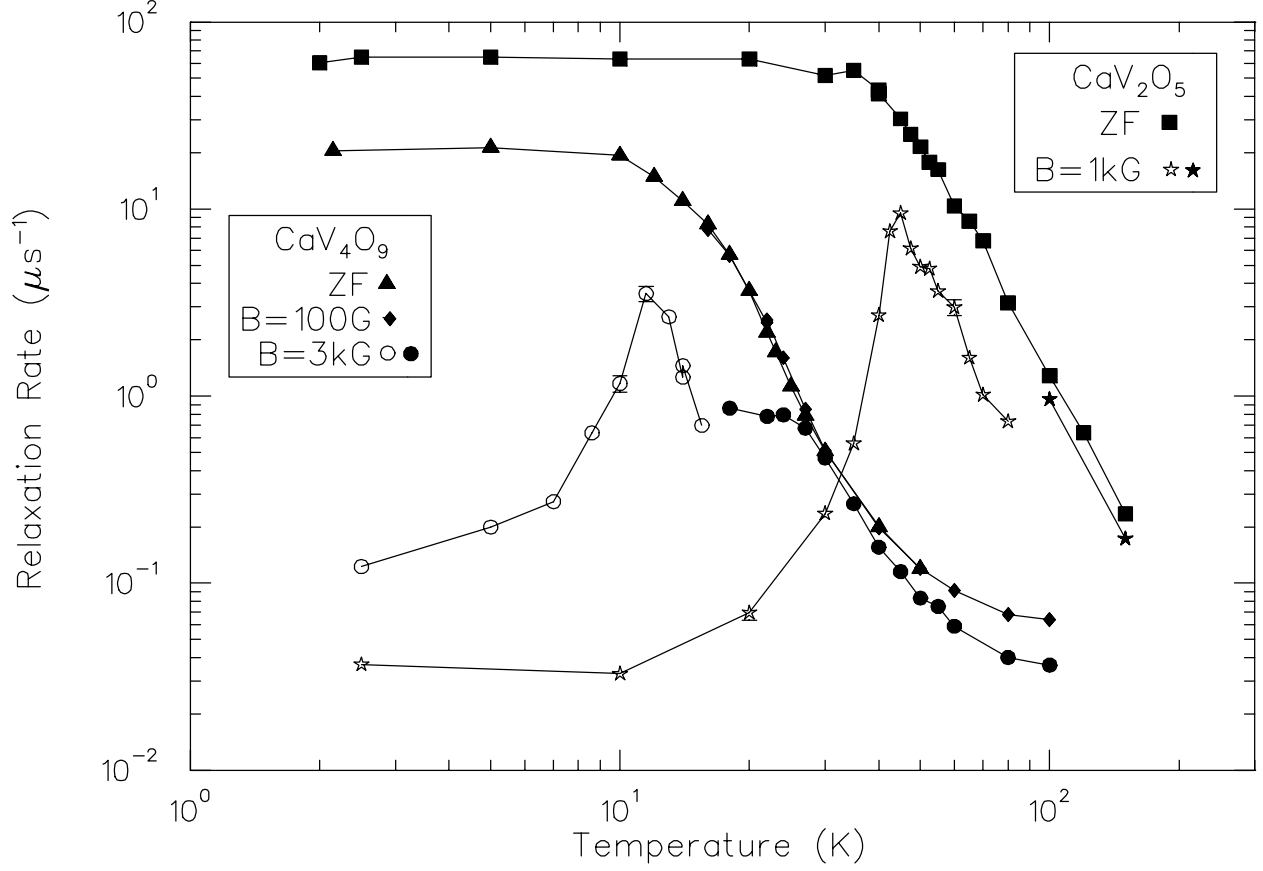


FIG. 3. Relaxation rate *vs.* temperature in: CaV_4O_9 , for zero field (triangles), 100 G (diamonds) and 3000 G (circles); CaV_2O_5 in zero field (squares) and 1000 G (stars). Open symbols indicate a two component relaxation function and correspond to the long-lived component which reflects dynamical ($1/T_1$) relaxation.

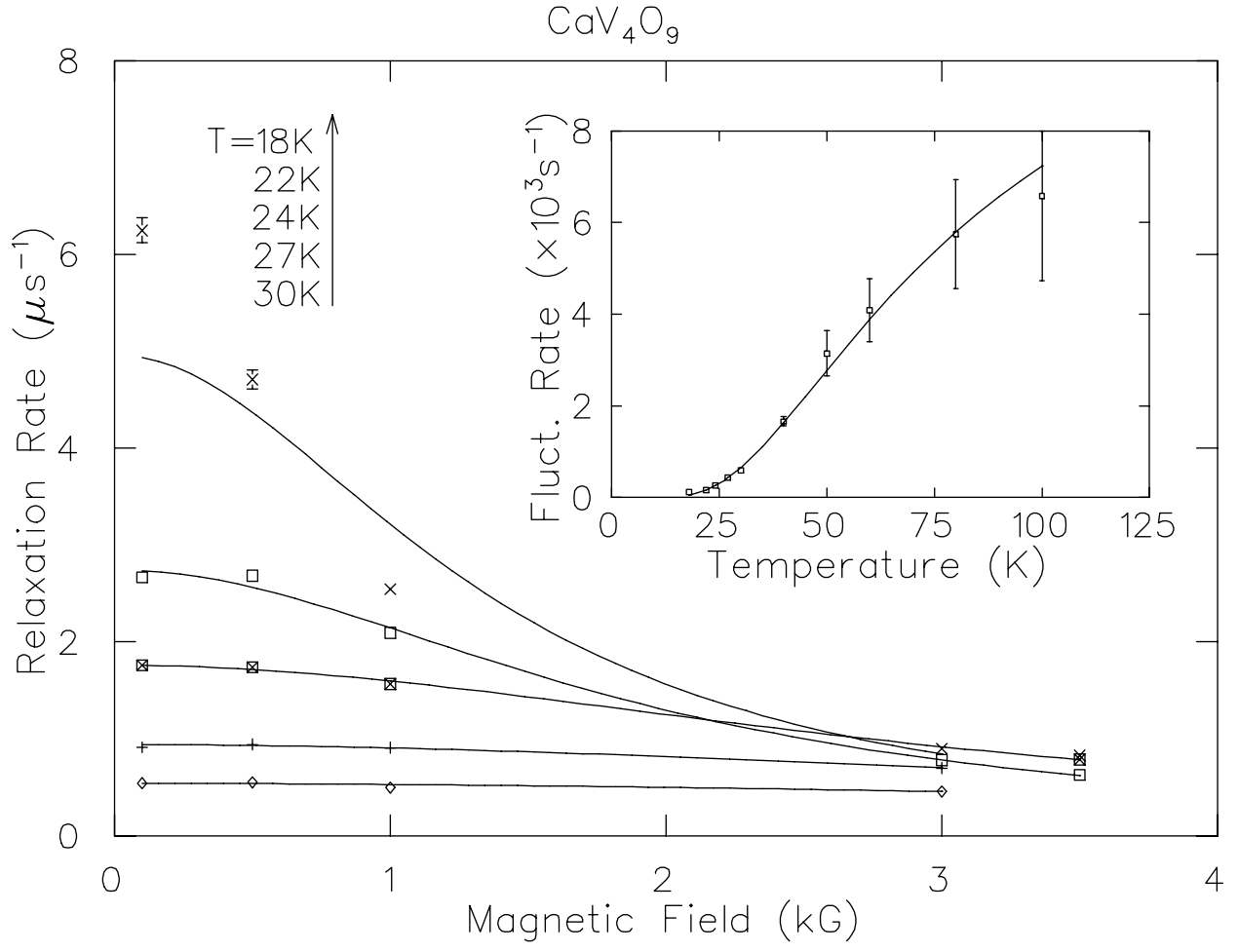


FIG. 4. $1/T_1$ Relaxation rate *vs.* field in CaV_4O_9 for $T=18$ K, 22 K, 24 K, 27 K and 30 K. Curve is fit to Eqn. 1. Inset: Field fluctuation rate from Eqn. 1.